

Evaluation of SESOIL (Seasonal Soil Compartment Model), PRZM (Pesticide Root Zone Model), and PESTAN (Pesticide Analytical Model) in a Laboratory Column Leaching Experiment

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EVALUATION OF SESOIL, PRZM AND PESTAN IN A LABORATORY COLUMN LEACHING EXPERIMENT

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Abstract—Four 2-m columns filled with sandy soil were loaded with six organic chemicals (dicamba, 2,4-dichlorophenoxyacetic acid, atrazine, diazinon, pentachlorophenol, and lindane) and watered for 30 d in a controlled laboratory experiment. Chemical migration was monitored by analyses of daily effluent samples and soil sample cores, the latter collected on day 30 from 5-cm compartments throughout each column. Observed chemical migration patterns were compared with the predictions of three vadose zone fate-and-transport models: SESOIL, PRZM and PESTAN. Two sets of comparisons with the observed data were conducted using input data either obtained from the literature or derived from laboratory measurements using the actual experimental chemicals and soil. Evaluations of model performance revealed substantial variability depending on the chemical type and model tested. PRZM and PESTAN showed greater improvement in prediction of observed chemical migration patterns with the use of measured input data than did SESOIL. The limitations of these models, if used for screening purposes without a priori measurement of chemical- and site-specific model input data or post hoc calibration with existing field data, should be recognized.

Keywords—Seasonal soil compartment model (SESOIL) Pesticide root zone model (PRZM)
Pesticide analytical model (PESTAN) Model validation

INTRODUCTION

The fate of organic pollutants in the vadose (unsaturated) zone has become an area of active research in recent years. Pollutant transport and transformation in the vadose zone are complex processes that are often difficult, as well as expensive, to measure. Although numerous models that simulate fate and transport through the vadose zone have been developed [1-5], little work has been done to "validate" these models, that is, to compare the results of model simulations with field measurements of corresponding environmental parameters. Any environmental fate and

transport model must be tested for predictive performance before it can generally be useful as an aid in regulatory decision making. Therefore, it has been recommended that high priority be given to experiments that attempt to validate existing models [6,7].

Testing of models can range in complexity from simple controlled laboratory tests to full-scale field tests on existing pollution problems. As model performance evaluation becomes more complex, it also becomes more costly and difficult to perform. As a result, most of the soil fate and transport model validations attempted to date have been small-scale laboratory experiments or have used published chemical data generated in other studies. In addition, most larger-scale validation attempts have concentrated on single rather than multipollutant problems [1,8]. In general, little has been done either in the laboratory or in the field to test the predictive capability of vadose zone models.

The present study was a performance evaluation of three vadose zone models. The models chosen for testing were developed for the U.S.

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Environmental Protection Agency (EPA) at the Environmental Research Laboratory in Athens, Georgia [4], at the R.S. Kerr Environmental Research Laboratory in Ada, Oklahoma [1], and at Arthur D. Little Incorporated in Cambridge, Massachusetts [3] with support from the EPA Office of Toxic Substances (OTS) in Washington, D.C. Little performance testing of these models has been published in the literature. Various experimental applications for the Athens pesticide root zone model (PRZM) have been reported [9-11], and current field testing is under way at that laboratory. The pesticide analytical model (PESTAN) developed at the Ada laboratory has been used in laboratory tests with small soil columns and against field data [1,8]. The seasonal soil compartment model (SESOIL) developed for OTS has been evaluated with data obtained from the literature [12,13].

In the present study, all three models (PRZM, PESTAN, SESOIL) were evaluated for their ability to predict the fate and transport of six organic chemicals in large soil columns over a 30-d period. Chemicals were applied to the surface of each soil column and leached throughout the study period. At the conclusion of the 30-d period, the columns were broken down and the distribution of the chemicals throughout the columns determined. In addition, chemical concentrations in leachate from the columns were monitored throughout the experiment. Comparisons of the observed concentrations of each chemical species in column leachate and soil samples were made with model simulations using input data obtained both from the available literature and from the laboratory-derived data. Conclusions regarding model performance, effectiveness of the use of literature-based model input data and effectiveness of laboratory-derived model input data are presented.

MATERIALS AND METHODS

Organic chemicals and soil

Six organic chemicals were chosen for testing: dicamba, 2,4-dichlorophenoxyacetic acid (2,4-D), atrazine, diazinon, pentachlorophenol (PCP) and lindane. The choice of chemicals was designed to test the models over a range of partition coefficients for compounds known to be relatively non-volatile. The choice was also influenced by the availability of other model input rate constant information (e.g., degradation), the existence of standard analytical methods and the degree of chemical toxicity. Degradation rates were mea-

sured over a 90-d period to verify that no significant chemical losses (particularly of 2,4-D) would occur during the shipping and storage of effluent and soil samples. All chemicals were tested for purity prior to introduction onto the soil columns [14,15].

The soil used in this study was a natural sandy soil (89.5% sand, 6.7% silt, 3.8% clay) shipped from Puyallup, Washington. Before the beginning of all experiments, homogeneity tests were conducted on randomly selected bags of soil to verify that all bags were well mixed and of a consistent texture and chemical type. The homogeneity tests measured calcium, magnesium, sodium, phosphorus and potassium concentrations, electrical conductivity, pH, percent total organic carbon, cation exchange capacity and sodium adsorption ratio. In addition, all soil was sieved through a 0.63 cm screen prior to column packing to remove any large rocks or other debris, further assuring a homogeneous mix in the column experiments.

Soil column design and construction

Five soil columns were constructed of polyvinyl chloride pipe with a 59.4 cm inside diameter and a 6-mm wall lined with Teflon. Columns were 240 cm tall and were placed on specially constructed bases (Fig. 1) fabricated of A-36 steel and composed of four parts: a main support ring, stabilizing base, sieve plate and collection chamber plate. A sample collection tube attached to the bottom of the collection chamber plate allowed the column to drain and the effluent to be collected. The sieve plate was covered with 0.5 cm of Pyrex spun glass to prevent soil from falling through the holes in the sieve plate. All welded joints were tested for water tightness and the base sealed to the column using silicon sealant.

Columns were installed in a greenhouse with glass panes that were whitewashed prior to the experiment to facilitate temperature control within the greenhouse. Each column was placed on a Mettler balance with a $1,500 \pm 0.02$ kg capacity and packed by successively delivering approximately 17-kg portions of soil to each column until the packing reached a height of 2 m. Each portion added was spread evenly over the column surface and tamped to a uniform consistency. All columns were packed by a single individual to decrease differences due to packing technique. The total weight of soil delivered to each column averaged 781.98 kg (± 8.73 kg). Initial moisture content was 8.59% ($\pm 0.35\%$).

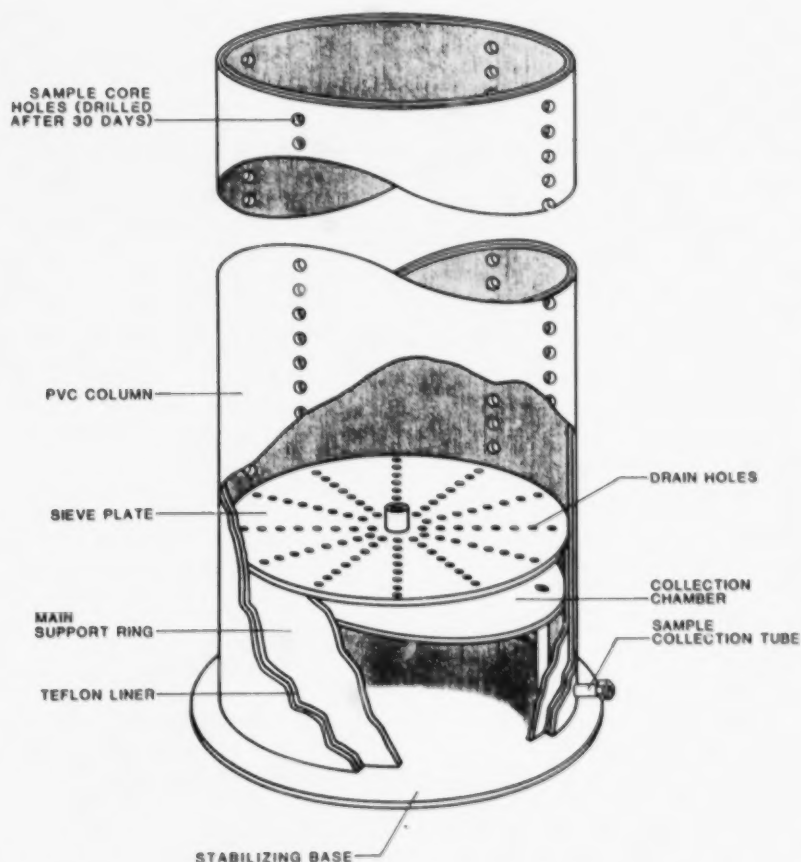


Fig. 1. Schematic of 2-m experimental soil columns.

Experimental design

Packed soil columns were initially saturated with deionized water by introducing water through the base sample collection tube (Fig. 1) until a thin film of water had risen to cover the column surface. Columns were then leached with deionized water by watering the surface of the columns from above until a consistently low conductivity (less than 30 μmhos) was observed in the column effluent. This procedure, which required application of approximately 508.0 cm of water over a 12-d period, was followed in order to minimize any potential analytical interference that might be associated with residual unbound salts in the soil.

Following column saturation and leaching, 250.5 mg of each of the six organic chemicals was

introduced onto the surface of four of the five columns in a soil-chemical mixture; the fifth column was used as a control. All six chemicals were mixed in 16 kg of air-dried soil. This mixture was spread over the surface of the columns, simulating an agricultural application of 9.1 kg of pesticide per hectare of soil. The contaminated soil was tamped to a uniform consistency; then 4 kg of uncontaminated air-dried soil was spread evenly over the column surface. The control column was loaded with 16 kg of uncontaminated soil and a 4-kg cap in the same manner.

Following loading, columns were watered with deionized water on a twice-daily schedule for 30 d. Deionized water was used as the best approximation of natural rainfall, since local water supplies were high in conductivity and salts. Both the

watering procedure and the use of an open-tank reservoir for water storage allowed the pH of the deionized water to equilibrate to that of "standard" rainwater by absorbing CO₂ from the air.

Each watering cycle was timed to deliver approximately 5.4 cm of water to the column surface over a 1-h period. Water was delivered to the column surface through a Spraying Systems brass, full-cone TG03 nozzle at 45 lb of pressure. The nozzle was positioned 57 cm above the soil surface to provide an even mist over the entire column surface. Timing of water delivery was controlled by an IBM-XT/Isaac 2000 combination microcomputer/laboratory interface system.

During the study both hardware and software problems developed that required intermittent water cycle adjustments throughout the study to ensure that all columns received the same total volume of water (280.2 ± 1.0 cm) over the 30-d period. The amount of water delivered to and passing through each column was monitored by recording the changes in weight of the columns before and after watering, and before and after effluent sampling. Data were collected using the IBM-XT/Isaac 2000 system.

Sample collection and analysis

Column leachate was collected once daily throughout the 30-d study period. In addition, triplicate water samples were collected from each column four times during the study for a quality assurance check of sample collection procedures. Leachate samples were collected in a 2-liter Pyrex glass primary collection chamber located near each column base. Effluent in this primary collection chamber was pumped dry every 30 min over 24 h into a compositing chamber using an ISCO water sampler equipped with Teflon tubing. The compositing chamber was maintained in an ice bath until daily composite samples were collected. Once daily, 2-liter subsamples of the composited 24-h sample were collected, packed in ice and shipped to the laboratory for analysis. The total volume of water collected in the compositing chamber was measured and recorded daily.

Soil samples were collected at 30 d by coring the columns at 5-cm depth increments. Holes were drilled at four sites located 90° apart on the column sides at each of 40 depths, located 5 cm apart down the column (Fig. 1). A stainless steel coring tube, 2.5 cm (1 in.) in diameter, was used to collect samples from the four sites on each column at each depth. All four cores from a given depth were composited into a single sample jar, packed in ice

and shipped to the laboratory for analysis. This procedure was repeated two times at five depths down each column, yielding triplicate composite samples for the quality assurance of sample collection procedures. The soil cap covering each column was sampled by scraping the column surface with a Teflon-covered spatula and placing the samples into glass jars. The control column was sampled in the same manner as were the experimental columns except that soil samples were located at 30-cm depths down the column rather than at 5-cm depths and that leachate samples were only collected for the first 7 d of the experimental period.

Deuterated spikes were added prior to sample analysis to both water samples and soil aliquots to determine extraction efficiency. All analyses were performed by GC-MS in the selected ion monitoring mode with a Finnigan 1020 instrument interfaced with an INCOS 2300 data system. Water samples were extracted at neutral pH in methylene chloride to isolate atrazine, diazinon, PCP and lindane, then acidified at a pH of less than 1 and extracted again to recover dicamba and 2,4-D and their corresponding stable-labeled isotopes. Soil samples were completely mixed with a spatula prior to analysis and then aliquots were removed [14,15]. Two extraction aliquots were separated for analysis: one aliquot was extracted at pH 1 to isolate dicamba, 2,4-D and PCP; the other aliquot was extracted at neutral pH to isolate atrazine, diazinon and lindane.

Model input data

When possible, model input values for the three models of interest were measured directly. Sorption, degradation and Freundlich exponent were determined in the laboratory for each test chemical [14,15]. Sorption and degradation tests were run with all six chemicals combined but at concentrations approximately one order of magnitude lower than the surface application rate. This was done to simulate the actual chemical concentrations in solution moving through the soil column during the 30-d experiment. Physical soil characteristics, including pH, bulk density, percent sand, silt and clay and percent moisture were measured using standard methods [16]. Percent organic carbon was measured using the Walkley-Black method [17]. Environmentally related parameters, including air temperature and relative humidity inside the greenhouse, were measured using a Weather Corporation Hygrothermograph; evaporation was measured using a National Weather Service Class A evaporation pan and micrometer

hook gauge. Albedo inside and outside the greenhouse was measured with a Weathertronics albedo probe (No. 3023) connected to the IBM-XT/Isaac system. Field capacity, defined as the water retention capacity of soils under one-third bar pressure [4], was measured using saturated surface cores from experimental columns placed in Tempe cells and subjected to one-third bar pressure to determine water loss. Hydrodynamic dispersion coefficient (d), as defined by the one-dimensional form of the advective-dispersion equation [18-21], was estimated by conducting subsequent chloride breakthrough studies on the large experimental columns and fitting these data to a nonlinear least-squares regression [22]. The curve coefficient input to PESTAN as a measure of moisture-holding capacity of the soil was estimated from a series of soil suction values ranging from saturation to one-third bar pressure generated with Tempe cell equipment [23].

Model simulation design

Frequently, users of modern soil fate and transport models are faced with exercising the models for screening purposes when they have little field parameter information or limited site-specific physical and chemical background measurements to compare with model simulations. In such scenarios, users must frequently input data for the chemical of interest, based upon general soil type, that has been obtained from some published source. For this reason, model simulations in the present study were conducted under two sets of conditions: (a) using model input values for chemical rate constants (and in some cases, for soil characteristics) obtained from the literature, and (b) using values experimentally determined in the laboratory based on the actual soil and test chemicals used in this project. This study design was implemented to determine to what extent PESTAN, PRZM and SESOIL model predictions would be altered by the use of "best guess" literature versus measured input information.

The selection of chemical rate constants for the "literature" model runs (Table 1) was based primarily on availability. If there was a choice of values for multiple sources, the most recent was used. If a range of values was given in a single reference, the geometric mean of the range was used. Values of parameters for which no data could be found were calculated from existing data using standard methods [24] where possible or estimated (for example, where no data on the Freundlich exponent were available, 1 was assumed). Selection of

literature-based soil and environmental properties was based on recommendations in the various models' documentation manuals. In all cases (both literature and measured runs), actual measured precipitation (daily volume of water added) for each column and soil composition (89.5% sand, 6.7% silt, 3.8% clay, 0.105% total organic carbon) were used.

In general, simulations were performed under the simplest conditions specified by each model's author and that reproduced actual laboratory experimental conditions. For both model simulation conditions, a mean monthly watering rate from the four experimental columns was used as the hydrology input for all models. Sensitivity analyses were conducted before beginning the experimental phase of the study to determine the relative effect of each input parameter on output predictions. No post hoc calibration to "best fit" any model's results to the observed soil and effluent concentration profiles was conducted.

PESTAN. PESTAN requires the user to input a specified minimum and maximum number of days to be modeled and the distance of chemical migration. The PESTAN output then divides these time and depth ranges into 40 increments. For this study, preliminary PESTAN runs were based upon 40 d and 200 cm as minimum time and depth values. This provided daily increment data for comparisons with measured chemicals in column effluent and soil samples. The initial runs revealed the predicted maximum depth of chemical movement for those chemicals that were still present in the soil profile on day 30. They also revealed the days on which pesticide breakthrough was predicted to occur for the faster-moving chemicals. To obtain a smoothed prediction curve containing numerous data points, it was necessary to perform additional simulations using smaller depth and time increments. This was accomplished as follows: For those chemicals that PESTAN predicted would move into the effluent in less than 30 d (e.g., dicamba), the required minimum and maximum depth input specifications were set to 199 and 200 cm, respectively (i.e., the bottom of the column). Minimum and maximum times were then set to spread over those days across which pesticide movement out the bottom of the column had been predicted to occur in the preliminary runs, for example, 4 to 7 d for dicamba. This procedure provided data that yielded a plot of chemical concentration in the leachate as a function of time. Similarly, for those chemicals initially predicted to remain in the soil column on day 30 (e.g., lin-

Table 1. Summary of rate constants and other model input data used in SESOIL, PRZM and PESTAN simulations, based on literature values and laboratory measurements

	Dicamba	2,4-D	Atrazine	Diazinon	PCP	Lindane
Adsorption coefficient (KOC) (μg/g/μg/ml)						
Literature	2.2 [24]	20 [24]	160 [24]	646 ^a	900 [26]	2,500 [24]
Measured	114	133	470	1,554	3,182	3,362
Desorption coefficient (KD) (cm ³ g ⁻¹)						
Literature ^b	0.002	0.021	0.168	0.678	0.945	2.625
Measured	0.120	0.140	0.493	1.632	3.341	3.53
Solubility (mg/L) ^c	4,500 [26]	900 [26]	33 [24]	40 [26]	14 [26]	7.8 [27]
Degradation rate (d ⁻¹)						
Literature	0.065 [4]	0.040 [4]	0.010 [4]	0.015 [4]	0.033 [26]	0.005 [4]
Measured	0.009	0.140	0.009	0.032	0.025	0.032
Freundlich exponent (n)						
Literature	0.85 [28]	1.33 [29]	1.14 [29]	1.00 ^d	2.38 [30]	1.02 [31]
Measured	1.12	0.96	1.36	1.11	1.21	1.23
Henry's Law constant ^e	1.29 × 10 ⁻⁹	1.939 × 10 ⁻¹⁰	7.29 × 10 ⁻⁹	1.40 × 10 ⁻⁶	2.8 × 10 ⁻⁶	7.8 × 10 ⁻⁶
Neutral hydrolysis rate constant ^c	0 ^d	0 ^d	0 ^d	4.3 × 10 ⁻⁸ [24]	0 [27]	0 [27]
Acid hydrolysis rate constant ^c	0 ^d	0 ^d	0 ^d	2.1 × 10 ⁻² [24]	0 [27]	0 [27]
Basic hydrolysis rate constant ^c	0 ^d	0 ^d	0 ^d	5.3 × 10 ⁻³ [24]	0 [27]	0 [27]
Molecular weight [32]	221.04	221.04	216.06	304.36	266.35	290.85
Soil characteristics						
	Bulk density (g/cc)	Porosity (cm ³ /cm ³)	Curve coefficient	Hydraulic conductivity	Dispersion coefficient (cm ² /h)	
Literature	1.57 [4]	0.35 [3]	4.0 [23]	63.0 [23]	0.03 [33]	
Measured	1.38	—	2.5	17.8	2.48	
	Field capacity (cm ³ cm ⁻³)	Wilting point (cm ³ cm ⁻³)	Intrinsic permeability (cm ²)	Disconnectedness index		
Literature	— ^f	— ^f	0.1 × 10 ⁻⁷ [3]	3.7 [34]		
Measured	0.148	0.0424	—	—		
Environmental conditions (average measured values)						
	Temperature (0°C)	Relative humidity (%)	Evaporation (cm/d)	Albedo	Watering rate (cm/d/surface area)	
	26.7	66.7	0.189	0.221	9.67	

^aCalculated from information in ref. 24.^bCalculated from KOC and percent organic carbon (0.105%) in experimental soil.^cLiterature values only.^dValue assumed; for rationale behind assumptions for the hydrolysis rate constants, see ref. 34.^eCalculated from chemical vapor pressure, solubility and molecular weight.^fIf no value is input into model, PRZM internally calculates based on percent sand, silt and clay in soil.

dane), the minimum and maximum times were set for 30 and 31 d, respectively. In this case, the predicted spread in centimeters of chemical in the soil profile was used to establish the minimum and

maximum depths, for example, 50 to 75 cm for lindane. Thus a series of 40 predicted points showing the concentration distribution of chemical in the soil columns on day 30 was produced. Alter-

ation of the depth and time minima and maxima did not change the overall results of the simulations but only provided sufficient points for plotting. Since the input decay rates required by PESTAN are defined on the basis of sorbed rather than total chemical concentration [25], degradation rates used for the PESTAN literature-based simulations were also adjusted prior to input. Additionally, all PESTAN simulations were rerun with the degradation rate set equal to zero to determine the "degradation component" in the model for mass balance calculations.

PRZM. For PRZM, model simulations were set to predict chemical movement over a 60-d period beginning on 15 July and ending on 15 September. Pesticide was applied (in the model) on 1 August. Fallow soil conditions were created for the 30-d experimental period (1 to 30 August) by setting crops to emerge, mature and be harvested in September. The input curve number, which affects intrinsic permeability in the model, was lowered until zero runoff was predicted to occur under the experimental "rainfall" conditions (column watering cycles). Thus, PRZM provided a predicted chemical profile on day 30 (30 August) to compare with measured chemical profiles from columns cored on day 30. It also provided daily degradation, daily amount of pesticide leached below the root zone (equivalent to the amount moving out of the columns in the leachate) and chemical mass remaining in the column on day 30, all of which were used for mass balance calculations.

SESOIL. For SESOIL, column predictions were compartmentalized into four equal-sized compartments, each 50 cm in depth. It was not possible to eliminate surface runoff in SESOIL as had been done in PRZM. Thus, some hydrological calibration was required to alter intrinsic permeabilities so that the predicted infiltration rate matched the actual amount of water applied to the soil columns, regardless of how much surface runoff was "occurring" according to model output. This procedure is recommended in the SESOIL user's manual [3].

SESOIL presents results on a monthly basis. Therefore, no SESOIL estimate of daily effluent concentration was output for comparison with observed daily effluent concentrations, although cumulative total chemical mass for the experimental period was estimated. In addition, it was necessary to perform calculations on simulated soil concentration output to allow comparison with observed chemical concentrations in the columns after 30 d of leaching. SESOIL outputs total mass in the soil and the soil-moisture fraction of each

compartment. Observed chemical concentrations represent a combination of adsorbed chemical and chemical resident in the soil moisture. To generate simulation data comparable with the observed chemical concentrations, the total mass for each compartment of adsorbed chemical plus chemical in the soil moisture was divided by the total mass of soil plus soil moisture in each compartment. SESOIL, in the present simulations, predicted an overall moisture content in the experimental columns of approximately 12%, which was close to that actually observed (median = 12.5%). It should be noted that the above calculations for comparison of SESOIL soil concentration output data with measured data would become increasingly invalid to the extent that increasing discrepancies were to occur between predicted versus measured percent moisture data.

RESULTS

Chemical analyses

Five columns were watered during the course of the 30-d laboratory experiment: one control column (No. 51), which was treated as the others were except that test chemicals were not added, and four columns (Nos. 52 to 55), to which 250.5 mg of each of the six test chemicals was added. There were never more than trace concentrations (0.1% or less of total grams added chemical) of the six test chemicals measured in either leachate or soil samples taken from control column 51.

For the four test columns (Nos. 52 to 55), three of the six test chemicals (dicamba, 2,4-D and atrazine) "broke through" during the 30-d study period, i.e., were found in detectable concentrations in daily leachate samples (Table 2). Dicamba was the first chemical to appear, with breakthrough on days 6 to 7. Breakthrough for 2,4-D occurred on days 10 to 12; atrazine was collected in leachate samples beginning on days 21 and 22. Diazinon, PCP and lindane were never measured in leachate samples from any column.

Of the total chemical mixture added to each column at the beginning of the project (250.5 mg of each chemical blended into 15.7 kg soil), dicamba was recovered in the greatest quantity, with 68 to 120% cumulative chemical recovery from the column leachate samples over the 30-d period (Table 2). There was 15 to 28% recovery of 2,4-D in the leachate samples, and 1 to 2% total recovery of the available atrazine mass. Coefficients of variation for all chemicals in Table 2 are based on the analysis of quality assurance triplicates from both leachate and soil samples; these provide

Table 2. Day of chemical breakthrough in effluent samples, cumulative mass of chemical in effluent over sampling period and cumulative mass of chemical in soil column on day 30

	Columns			
	52	53	54	55
Dicamba (C.V. = 30.4%)				
Breakthrough day	6	7	7	7
Effluent mass (mg)	175.9 (70%)	219.2 (88%)	170.0 (68%)	301.6 (120%)
Soil total mass (mg)	—	—	—	—
2,4-D (C.V. = 25.4%)				
Breakthrough day	10	12	11	11
Effluent mass (mg)	41.7 (17%)	45.0 (18%)	37.2 (15%)	70.9 (28%)
Soil total mass (mg)	—	—	—	—
Atrazine (C.V. = 21.5% soil, 5.2% effluent)				
Breakthrough day	21	21	23	23
Effluent mass (mg)	2.7 (1%)	6.1 (2%)	2.6 (1%)	4.5 (2%)
Soil total mass (mg)	112.7 (45%)	99.2 (40%)	83.2 (33%)	84.2 (34%)
Diazinon (C.V. = 23.5%)				
Breakthrough day	—	—	—	—
Effluent mass (mg)	—	—	—	—
Soil total mass (mg)	55.9 (22%)	58.1 (23%)	37.8 (15%)	36.8 (15%)
PCP (C.V. = 46.1%)				
Breakthrough day	—	—	—	—
Effluent mass (mg)	—	—	—	—
Soil total mass (mg)	99.4 (40%)	94.7 (38%)	53.0 (21%)	57.8 (23%)
Lindane (C.V. = 23.2%)				
Breakthrough day	—	—	—	—
Effluent mass (mg)	—	—	—	—
Soil total mass (mg)	192.6 (77%)	192.7 (77%)	173.1 (69%)	160.1 (64%)

Percentage of total mass initially loaded onto column in parentheses; average coefficients of variation (C.V.) based on analysis of quality assurance field replicates.

an estimate of the variance associated with the field collection technique.

Analysis of soil cores taken on day 30 from 5-cm depth compartments throughout the columns revealed that four of the test chemicals (atrazine, diazinon, PCP and lindane) remained in the columns in detectable concentrations. Between 33 and 45% of the original atrazine was recovered from the soil in addition to that measured in leachate samples (Table 2). Diazinon, PCP and lindane were recovered from the soil columns in percentages ranging from 15 to 23% for diazinon, 21 to 40% for PCP and 64 to 77% for lindane.

Model simulations

Mass balance calculations for each model and chemical were compared with the measured chemical data (Table 3). In general, the combination of predicted soil, leachate and degradation components accounted for 100% of the original chemical loading in all model simulations. It can be seen, however, that individual model "performance," in terms of predicting chemical mass distributions observed in the column experiments,

was highly chemical-specific for each model. For example, in the literature-based runs, all three models predicted that more than 90% of the available lindane would be distributed throughout the soil compartment of the columns. This predicted mass was higher than the mean sorbed lindane measured in the four test columns (179.6 mg = 72% of total available lindane); nevertheless, all three models produced a relatively realistic predicted lindane distribution. On the other hand, in literature-based runs for atrazine, all three models predicted that the bulk of chemical would leach through the columns more quickly than was actually observed in the laboratory experiments, and all three models overestimated the atrazine leachate component. Only SESOIL predicted that atrazine would remain in the soil compartment at the end of 30 d. Similar observations could be made upon examination of the data presented in Table 3 for the remaining four chemicals in the literature-based model simulations. It should be noted that 95% confidence intervals around the actual observed column data points were in some cases large enough to result in overlap with the

Table 3. Mass balance calculations for measured chemical data (average from four columns) vs. PESTAN, PRZM and SESOIL model predictions, showing cumulative mass (mg) in soil, leachate and degradation components on day 30 (based on 250.5 mg initial loading)

	Literature runs			Measured runs		
	Soil	Leachate	Degradation	Soil	Leachate	Degradation
Dicamba						
PESTAN	—	22.0	228.4	—	169.6 ^a	80.5
PRZM	—	214.9	35.6	—	233.9	16.5
SESOIL	21.6	190.0	38.9	56.0	189.0	5.2
Measured	—	216.7 (± 96.6)	33.8 ^a	—	216.7 (± 96.6)	33.8 ^a
2,4-D						
PESTAN	—	82.8	167.8	—	4.3	246.3
PRZM	—	221.0	29.4	—	81.5	168.9
SESOIL	30.1	196.0	24.4	45.1	138.0	66.7
Measured	—	48.7 (± 24.1)	201.8 ^a	—	48.7 (± 24.1)	201.8 ^a
Atrazine						
PESTAN	—	242.4	8.1	2.0	189.5	58.9
PRZM	—	231.3	29.1	4.8	210.0	35.5
SESOIL	80.1	165.0	5.4	164.6	82.4	3.4
Measured	94.8 (± 22.2)	4.0 (± 2.6)	151.7 ^a	94.8 (± 22.2)	4.0 (± 2.6)	151.7 ^a
Diazinon						
PESTAN	—	246.5	7.0	152.2	—	98.2
PRZM	4.8	18.7	226.9	96.7	0.9	152.8
SESOIL ^b	164.9	65.8	5.2	213.8	13.3	5.6
Measured	47.2 (± 18.2)	—	203.3 ^a	47.2 (± 18.2)	—	203.3 ^a
PCP						
PESTAN	105.0	—	157.4	203.0	—	47.2
PRZM	71.1	29.1	150.2	120.4	—	130.0
SESOIL	247.0	0.3	3.6	248.2	0.5	2.0
Measured	76.2 (± 38.5)	—	174.3 ^a	76.2 (± 38.5)	—	174.3 ^a
Lindane						
PESTAN	238.3	—	13.2	192.6	—	57.4
PRZM	215.6	—	34.8	96.4	—	154.0
SESOIL	244.1	4.8	1.2	247.5	0.3	2.3
Measured	179.6 (± 25.4)	—	70.9 ^a	179.6 (± 25.4)	—	70.9 ^a

95% confidence limits about the average measured data in parentheses ($p = 0.05$).

^aChemical unaccounted for in either observed effluent or soil samples is assumed lost to degradation; see Table 2 for individual column mass balance information.

^bShows 14.3 mg volatilized in literature runs, and 17.6 mg from hydrolyzed chemical in soil and moisture in measured runs.

model-predicted masses for each chemical and compartment.

If the key rate constant model input information (e.g., degradation and sorption rates) were modified to more accurately reflect actual soil and laboratory environmental conditions, it might be expected that model performance would improve. In fact, for some chemical-model combinations in the "measured" model simulations, such was the case. For example, in the measured dicamba runs (Table 3), the PESTAN prediction for chemical lost to degradation was greatly reduced, resulting in all three models' accurately predicting that the bulk of chemical would be found in the column leachate samples. In the case of atrazine, all three measured model runs showed chemical remaining

in the soil compartment, although only SESOIL correctly predicted the magnitude of chemical measured in the column soil samples. However, it is clear from Table 3 that the use of measured input data, rather than literature-derived values, did not unequivocally improve the match between model predictions of mass balance and observed column data. Chemical- and model-specific variability still characterized the results.

Graphical comparisons of "literature" and "measured" model simulations with observed column effluent and soil data are presented in Figures 2 and 3. Darkened lines on the figures show model results, which are based on an average monthly watering rate from all columns. For purposes of comparison, the effluent and soil data from each

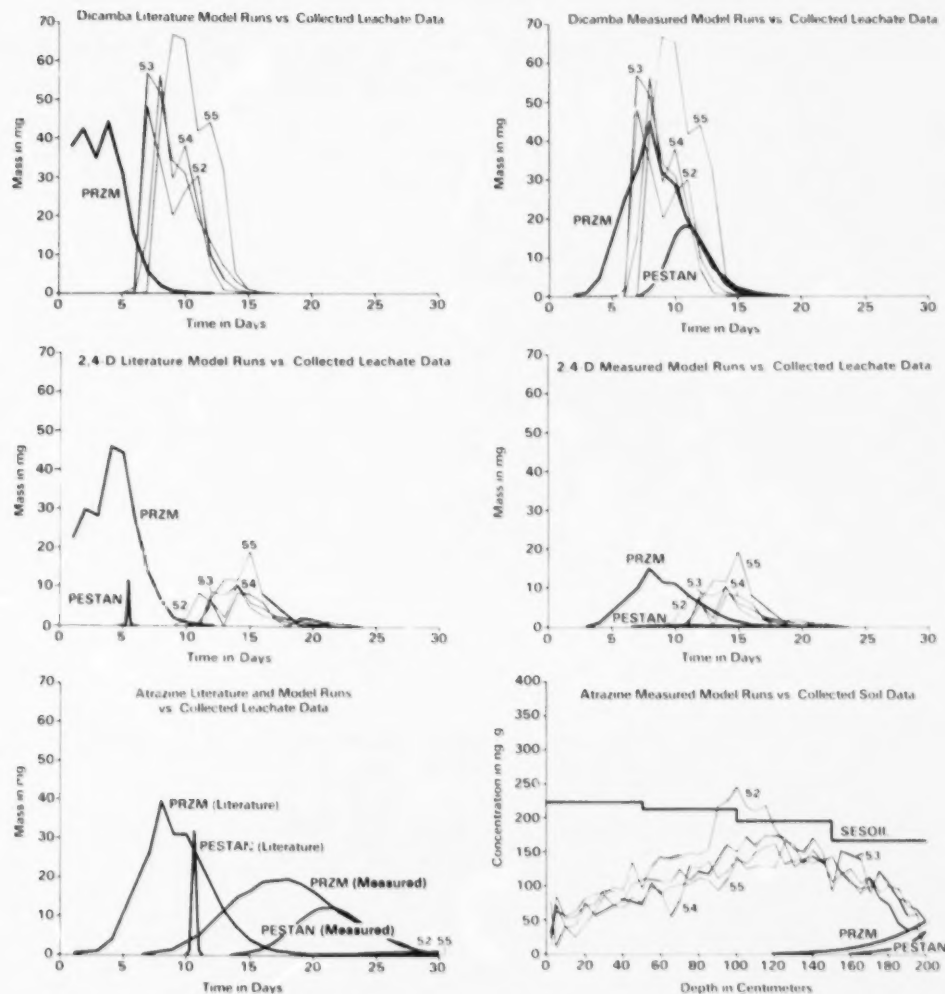


Fig. 2. Results of PRZM, PESTAN and SESOIL "literature" and "measured" model simulations compared with column data for dicamba, 2,4-D and atrazine.

of the four column replicates are presented rather than a single mean curve. This permits the reader to see at a glance not only differences and similarities in observed versus predicted chemical peaks and distribution patterns but also the replicate variability associated with the individual column data. Similar to the results noted above for the mass balance calculations, there was a trend for the models to "perform" better, i.e., to more closely approximate actually observed chemical peak location, height and distribution, when measured rate constant information was used rather

than literature-derived values (Figs. 2 and 3). However, once again, the extent of this improvement varied with chemical and model.

The most important example of this variation can be seen with the SESOIL predictions which, in general, did not improve with the use of literature-derived rate constant information. In this case, plots were restricted by some idiosyncratic characteristics of the model's design at the time this study was conducted: SESOIL assumed that once a chemical reached the top of any given compartment, there was instantaneous dispersion at equal

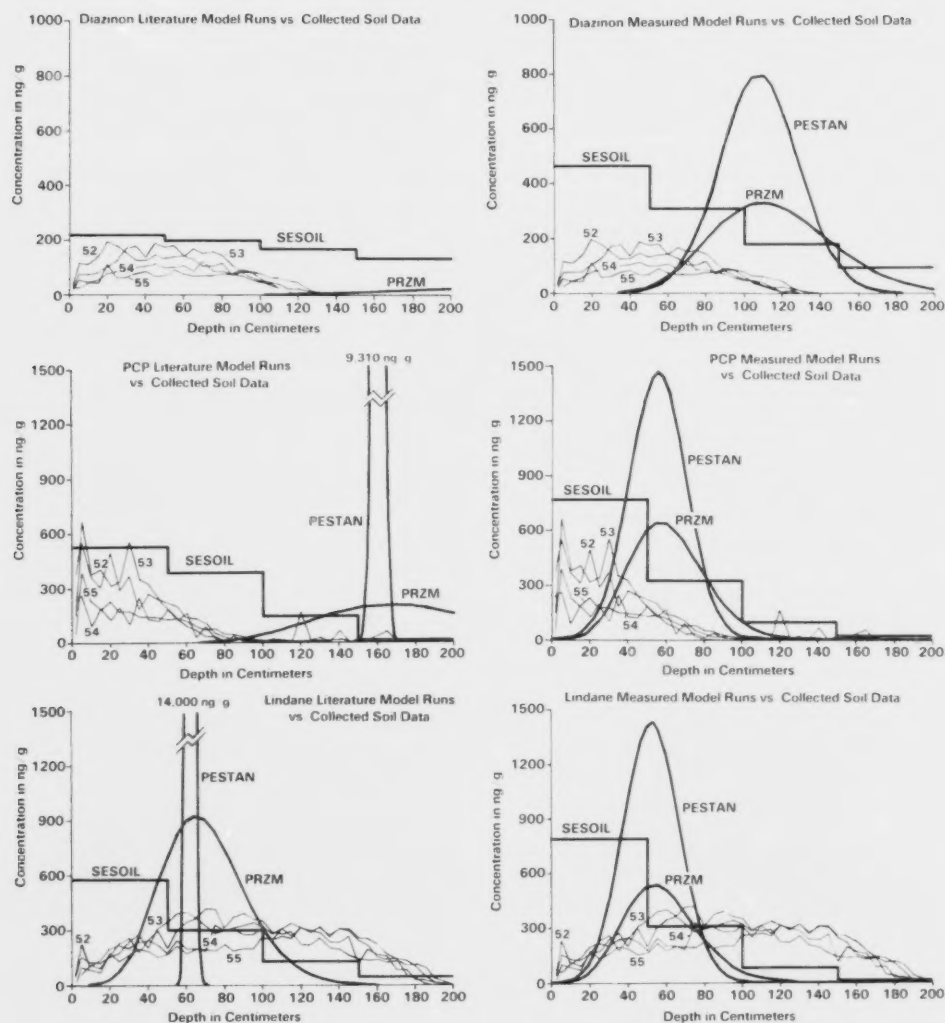


Fig. 3. Results of PRZM, PESTAN and SESOIL "literature" and "measured" model simulations compared with column data for diazinon, PCP and lindane.

concentrations of that chemical through the entire compartment. Furthermore, only four compartments could be defined between surface and ground water. Thus, graphical representations of the differences between literature and measured model simulations were less meaningful for SESOIL than for the other two test models.

It should also be noted that, in some cases, model simulations for a given chemical or medium could not be presented in these figures. For example, SESOIL only outputs a monthly total chemi-

cal mass predicted to move into "ground water." Thus, no curves for dicamba, 2,4-D or atrazine based upon daily mass of chemical predicted in the column leachate samples could be created. No PESTAN curve for the dicamba literature run is shown, since that model predicted virtually all chemical to be lost to degradation. Similarly, neither PESTAN nor PRZM predicted any chemical remaining in the soil column using literature-based rate constant information, so that figure is excluded, despite the fact that atrazine was the only

chemical that was found in both leachate and soil samples from the actual test columns.

DISCUSSION

The present study was undertaken to provide a performance evaluation of three vadose zone fate-and-transport models (SESOIL, PRZM, PESTAN) under a specified set of environmental conditions. It was noted in the Introduction that few attempts have been made in the literature to compare model simulations with field measurements of corresponding environmental data, despite the interest in using such models for screening and regulatory purposes. The present study sought to conduct such a comparison with six organic chemicals under simplified conditions in which precipitation, soil homogeneity and moisture content and external environmental conditions (such as temperature) were carefully controlled. To the extent that vadose zone models are designed to simulate field-scale conditions that are not characterized by homogeneous soil or meteorological conditions, this study did not provide a conclusive, final validation test. However, results of this study *do* clearly demonstrate the problems of taking site-specific predictions at face value without either a priori knowledge of the sites and chemicals being modeled or post hoc calibration of model input parameters to provide a more realistic output match to environmental conditions.

This study primarily sought to address the first of these two issues. The principal way it did so was to compare model simulations based on input information derived from literature sources with predictions based on input parameters measured in the laboratory. In some cases, differences between "best-guess" literature and laboratory-derived model input data were dramatic. For example, literature-based adsorption coefficients for dicamba and 2,4-D were 2.2 and 20 $\mu\text{g/g}/\mu\text{g/ml}$, respectively; measured values were 114 and 133 $\mu\text{g/g}/\mu\text{g/ml}$, respectively (Table 1). Another important difference in literature versus measured input values was seen with the dispersion coefficient, which was 0.03 cm^2/h for the literature model runs and 2.48 cm^2/h for the measured runs. Since both sorption and dispersion were highly sensitive parameters for the models examined, these differences greatly influenced the models' apparent predictive performances (Figs. 2 and 3). When the measured data were used, PRZM predictions for dicamba overlapped the observed effluent concentration curves; 2,4-D predictions were also greatly improved. For PESTAN, predicted soil concentration profiles using literature

values grossly underestimated the observed dispersion of both PCP and lindane throughout the columns. In fact, for PCP, both PESTAN and PRZM predicted chemical profiles more closely resembling the observed soil data when measured input data were used.

The above examples are good illustrations of the problems that may arise in applying vadose zone models in site-specific screening. It is clear from these data, however, that were post hoc calibration of PESTAN and PRZM input parameters to be performed, a fairly good "match" between predicted and observed data could be achieved in most cases. Recall that no calibration was applied to any model for this study unless such calibration was necessary to recreate the actual column environmental conditions (e.g., absence of surface runoff, fallow crop conditions). Thus, it must be reiterated that, ultimately, evaluation of model performance must be left to the judgment of each user and will vary with experimental characteristics. Individuals using the models merely to determine the probabilistic behavior of the chemical in the environment within a given range of environmental and chemical properties would have less need of rigorous prediction accuracy than would a regulatory agency attempting to predict a specific chemical hazard at a specific site. A user in the latter category may very well be applying the model of interest for the a priori screening of a new chemical or in a contaminated area where little data exist against which to calibrate. Based upon the results of the present study, such a user would be strongly advised to analytically determine as many input parameters as possible rather than rely strictly on available literature data.

A few closing remarks can be made about this model performance study. As previously stated, vadose zone models are not generally designed to model chemical movement through soil columns but rather are designed to simulate larger scale-field conditions. This column study attempted to provide a simplified test of the models with as few sources of field variation as possible. In so doing, it was recognized that the elimination of natural environmental variability reduced to some extent the data's representativeness of chemical behavior in an undisturbed field soil. This loss of representativeness, however, must be weighed against the cost of the great analytical variability that is inherent in more complex field studies. In other words, the present study attempted to test the models under simplified field conditions when sufficient replication would be feasible.

The question might also be raised as to whether

model distribution trends would have simulated observed results in this experiment more closely if the study had been extended over a period longer than 30 d, particularly for those chemicals (diazinon, PCP, lindane) with larger partition coefficients. It should be noted, however, that, although this experiment was of limited duration, the total volume of water applied to each column during the experimental period was large (average 280.2 cm). Since precipitation is the driving force behind chemical movement in these models, the chemical transport observed in the present 30-d study should be similar to that which would occur over an extended period of time with a lower daily rainfall.

CONCLUSIONS

The use of laboratory-derived input data and rate constants in many cases improved the performance of the PRZM and PESTAN models but generally did not improve the performance of SESOIL. Substantial variability in performance prediction results was observed for the chemicals and models. Tests indicate that PESTAN, PRZM and SESOIL need to be calibrated post hoc with measured, site-specific data before they are used for definitive predictions of the potential hazards of the introduction of site-specific chemicals into the vadose zone. If the models are used for a priori screening of new chemicals or in contaminated areas where little data exists against which to calibrate the models, the models' limitations under these conditions should be recognized. Caution should be used when drawing conclusions based on the models' results.

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